

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY


(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 14 SEP 2005

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Applicant's or agent's file reference 58688WO003		<b>FOR FURTHER ACTION</b>		See Form PCT/PEA/416
International application No. PCT/EP2004/006220		International filing date (day/month/year) 09.06.2004	Priority date (day/month/year) 13.06.2003	
International Patent Classification (IPC) or national classification and IPC C04B41/50				
Applicant 3M ESPE AG et al.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (Indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand  13.01.2005		Date of completion of this report  13.09.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Russell, G  Telephone No. +49 89 2399-8738		



# INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.  
PCT/EP2004/006220

## Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3 and 23.1(b))
- ☐ publication of the international application (under Rule 12.4)
- ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

### Description, Pages

1-17 as originally filed

### Claims, Numbers

1-18 filed with telefax on 02.09.2005

### Drawings, Sheets

1/1 as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify):*
- ☐ any table(s) related to sequence listing *(specify):*

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify):*
- ☐ any table(s) related to sequence listing *(specify):*

\* If item 4 applies, some or all of these sheets may be marked "superseded."

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-18
	No: Claims	
Inventive step (IS)	Yes: Claims	1-18
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-18
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**Re. Item V:**

1. Relevant cited prior art:

- D1: EP-A-0 230 534
- D2: DATABASE WPI Section Ch, Week 199510 Derwent  
Publications Ltd., London, GB; Class A97, AN 1995-070145 &  
JP-A-06 345566
- D3: DE-A-31 09 927
- D4: US-B-6 464 765
- D5: DE-A-199 04 522
- D6: DE-A-196 19 165
- D7: US-A-2 807 555

2. Novelty and inventive step

2.1 D1 (EP-A-0 230 534) claims a coloured metal salt glaze solution for screen printing ceramics with diffuse coloured patterns, said solution containing organic solvents and polymers as thickeners (claim 1).

In detail, the metal salt solution comprises preferably 10-40 wt.-% metal salt, 30-80 wt.-% of organic solvent, and 1-20 wt.-% of thickening agents (col. 3, l 20-22).

Example 1 explicitly describes such a solution comprising a high molecular weight (MW = 35.000) polyoxyethylene (i.e., PEG) present in an amount of 15 wt.-%, solvent, and a copper metal salt in an amount of 35 wt.-% based on the total weight of the composition.

Thus, the amount of metal ion is outside the range of claim 1 of the application.

Further, from the general teaching of D1 the skilled person has to make a number of choices starting from the Example to arrive at the subject-matter of the application: choose 1-8 wt.-% PEG; choose 0.01-7 wt.-% of metal salt.

D2 (JP-A-06 345566) discloses a colour pigment for glaze of ceramics comprising (a) fine particles of colour pigment loaded with (b) inorganic electrolyte e.g. alkali metal salt and water soluble polymer, and (c) polyethylene oxide (Abstract).

Polyethylene oxide is stated in the Japanese document to belong to the water-soluble polymers having a molecular weight of 100.000 to 2.000.000, most preferably used in an amount of 0.1-10 wt.-% ([0005]).

In Example 1 ([0007]) a colouring solution is described comprising water, calcium

chloride, 2 wt.-% of a sodium polyacrylate salt, and 2 wt.-% polyethylene oxide. Hence, the subject-matter of the application is novel over D2 due to the narrower molecular weight range of the PEG component c).

D4 (US-B1-6 464 765) relates to a *slurry* for decorating ceramic substrate e.g. porcelain tile, comprises solid particles of color-contributing metal salt dispersed in a saturated solution of color-contributing metal salt (claim 1). The slurry may also contain additives comprising 2-7 parts by weight polyethylene glycol 200 (claims 10, 12). The Examples describe slurries comprising 70 parts by weight metal complex, water as solvent, and 5 parts by weight PEG 200.

In contrast to the application, D4 describes slurries rather than a solution; only PEG of molecular weight 200 is disclosed.

Hence, the subject-matter of claims 1 to 18 is novel over the most relevant cited prior art D1 to D3 in accordance with the requirements of Article 33(2) PCT.

- 2.2 D1 and D2 describe metal salt solutions for colouring ceramic substrates comprising polyethylene glycol, and also consider the problem of colouring intensity, appearance, and homogeneity. D2 has the most technical features in common with the application and can, therefore, be considered as the closest prior art.

The distinguishing feature of the application over D2 is the molecular weight of the PEG component employed in the solution.

The applicant has shown by way of experimental data that a solutions comprising PEG having a Mn in the range 10.000-50.000 (specifically 35.000) are more suitable regarding homogeneous penetration of a low viscosity colour solution into ceramics without detrimentally affecting the deformation during firing compared to higher molecular weight PEG (Comparative Tests - Solution 1). D2 gives no suggestion to lower the molecular weight of added PEG.

Hence, the objective problem can be seen to provide ceramic colouring solution having improved penetration into the ceramic framework compared to those solutions of the art.

That these results can be achieved using a particular PEG of Mn 10.000-50.000 in an

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(SEPARATE SHEET)**

International application No.

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amount of 1-8 wt.-% is not obvious from the cited disclosures.

It is noted in addition, a solution containing 15 wt.-% PEG (Mn = 35.000 - as is the case in D1) does not result in a homogeneous coloured ceramic framework due to its higher viscosity. D4, while pertaining only to slurries, only explicitly discloses PEG 200.

Therefore, an inventive step can be acknowledged under Article 33(3) PCT.

## Claims

1. Solution for colouring ceramic framework, comprising:

a) a solvent

b) a metal salt or metal complex, soluble in the solvent, wherein the amount of the metal ions in the solution is in the range of 0,01 to 7,0 % by weight,

c) polyethylene glycol having a Mn in the range of 10.000 to 50.000 in an amount of 2 to 8 % by weight of the total composition,

d) optionally a stabilizer,

wherein the metal salt is selected from rare earth elements and/or of the subgroups of the rare earth elements and/or salts of transition metals of the groups IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB.

2. Solution according to claim 1, wherein the solution has a viscosity comparable to an aqueous polyethylene glycol solution (6 % by weight of polyethylene glycol 35.000 (Mn = 14.000 to 19.000) at 23°C.

3. Solution according to anyone of the preceding claims, wherein the solvent comprises water, methyl alcohol, ethyl alcohol, iso-propyl alcohol, n-propyl alcohol, acetone, glycol, glycerol alone or in admixture.

4. Solution according to anyone of the preceding claims, wherein the anion of the metal salt or metal complex is selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ .

5. Solution according to anyone of the preceding claims, wherein the metal salt or metal complex contains elements selected from La, Pr, Er, Fe, Co, Ni, Cu or Mn.

6. Solution according to anyone of the preceding claims, comprising additives selected from stabilizers, complex builders, beating additives buffers or thixotropic substances.
- 5 7. Process for obtaining a coloured ceramic framework, comprising the steps
  - a) providing a ceramic framework
  - b) providing a solution as described in anyone of the preceding claims.
  - c) treating the ceramic framework with the solution of b)
  - d) optionally drying the treated ceramic framework
  - 10 e) firing the treated ceramic framework.
8. Process according to claim 7, wherein the ceramic framework is treated with the solution for about 1 to 5 minutes at room temperature.
9. Process according to claim 7 or 8, wherein the firing takes place for a  $\text{ZrO}_2$  based ceramic at a temperature above  $1300^\circ\text{C}$  and lasts for at least 0,5 h and for a  $\text{Al}_2\text{O}_3$  based ceramic at a temperature above  $1350^\circ\text{C}$  and lasts for at least 0,5 h.
- 15 10. Process according to anyone of claims 7 to 9, wherein the firing takes place at a temperature above  $1300^\circ\text{C}$ .
11. Process according to anyone of claims 7 to 10, wherein colouring the ceramic framework is achieved by dipping the framework into the solution or applying the solution to the framework is achieved by spraying, brushing or by using a sponge or fabric.
- 20 12. Ceramic framework, treated with a solution as described in anyone of claims 1 to 6.



13. Ceramic framework according to claim 12, wherein the ceramic is presintered and adsorbent.
14. Ceramic framework, obtainable from a process as described in anyone of claims 7 to 11.
- 5 15. Ceramic framework according to anyone of claims 12 to 14 comprising  $\text{ZrO}_2$  or  $\text{Al}_2\text{O}_3$ .
16. Use of a solution as described in anyone of the claims 1 to 6 for treating a ceramic framework.
- 10 17. Use of a solution as described in anyone of the claims 1 to 6 for reducing the sintering deformation of ceramic framework during firing.
18. Use according to claims 16 or 17, wherein the ceramic framework is selected from presintered bodies comprising  $\text{ZrO}_2$  and/or  $\text{Al}_2\text{O}_3$ .